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(54) Title: METHOD, COMPOSITION AND TESTING DEVICE FOR THE QUALITATIVE AND
QUANTITATIVE DETERMINATION OF PEROXIDES, IN PARTICULAR, HYDROGEN PEROXIDE

(57) Abstract

The invention relates to a method, composition and a testing device for the qualitative and quantitative determination of peroxides, in particular, hydrogen peroxide in gases and liquids, using an analytical reaction which consists of two steps. In the first step, hydrogen peroxide or another peroxide induces a reaction, in which a titanium or iron compound is converted into a reaction product. In the second step, a dye is subjected to a dye decomposition reaction by the reaction product which resulted from the first step. According to the invention, it is possible not only to determine, in particular, hydrogen peroxide in the liquid phase, but also in the gaseous phase.

METHOD, COMPOSITION AND TESTING DEVICE FOR THE QUALITATIVE AND QUANTITATIVE DETERMINATION OF PEROXIDES, IN PARTICULAR OF HYDROGEN PEROXIDE

DESCRIPTION

The invention relates to a method, a composition and a testing device for the qualitative and quantitative determination of peroxides, in particular of hydrogen peroxide, in gases and liquids with the use of an analytical reaction that consists of two steps.

In analyzing for hydrogen peroxide one often uses a dye reaction in order to be able to follow chemical-biological processes, like for example the decomposition of glucose in blood, etc. For these one mainly uses reactions based on enzymes. Numerous documents describe reaction indicators that can be employed here, one can divide these into single component or dual component reaction indicators.

For example, US 3630847, DE-A1 36 25 852 (US 4800169) and DE-A1 24 60 903 (US 4385114) deal with single component reaction indicators. Dual component reaction indicators are described, for example, in US 3979262 and US 4492754.

The US patent 4855228 teaches a different manner. There, dye reactions are described, these dyes function based on redox-indicators. Here, a large amount of azo dyes is used, said azo dyes can be oxidized by hydrogen peroxide and change color when they are oxidized.

Additionally, a recognized analytical method for determining hydrogen peroxide and its adducts in aqueous systems is also known, in said method titanium ions are photometrically analyzed. This method has been instituted into a DIN standard (DIN 38409-H15). Hydrogen peroxide forms here with titanium ions a peroxo complex that has a degree of yellow coloring depending on the peroxide concentration. This reaction is also used as a qualitative analysis for hydrogen peroxide.

The processes and methods known up to now all have the same disadvantage in that they are limited to the determination of hydrogen peroxide in aqueous, and correspondingly, liquid systems. The known reactions catalyzed by enzymes are mostly selective to hydrogen peroxide or peroxides, however, they suffer from a lack of temperature stability, shelf-life stability and insensitivity towards disturbances. The analysis systems based on redox-indicators are not selective towards hydrogen peroxide, and correspondingly, to peroxides. In the described DIN method a yellow complex is generated which is neither light nor heat stable, nor does it last for some time, such that the result of the reaction cannot be directly documented.

The objective of the present invention is to demonstrate an improved manner in which peroxides and especially hydrogen peroxide can be detected and/or quantitatively determined not only in liquids, but rather also in gases.

This objective is solved by what the claims teach.

With the invented method it is possible to selectively detect and/or to quantitatively determine hydrogen peroxide or other peroxides and their decomposition products. The analysis is possible here in a wide temperature range, where the result of the reaction can be documented.

In particular the detection/analysis of hydrogen peroxide can also take place in the gaseous phase. In an inventive manner it is also especially possible to detect/analyze hydrogen peroxide vapors. This signifies a significant advantage over the known methods from the state of the art.

The invented method is based on an analytical reaction that consists of, or correspondingly, is constructed from two steps. The first step and correspondingly, the primary reaction is induced by hydrogen peroxide or other peroxides. As reactive components one uses here in particular an inorganic titanium compound or in particular an inorganic iron compound. As a preferred iron compound one employs an iron (II) compound and in particular ammonium iron(II) sulfate hexahydrate. As a preferred titanium compound one uses a titanium (IV) compound and in particular titanium (IV) oxide sulfate – sulfuric acid complex hydrate.

In the first step one or several reaction products are generated, from which one reaction product then in the second step, or correspondingly, in the secondary reaction induces a dye decomposition reaction which is in particular unambiguous and irreversible. This dye decomposition reaction can lead to the disappearance of the original color or its change. In the second step also more than one dye can be present, said dye succumbs to a dye decomposition

reaction. Additionally, other dyes and pigments can also be present which do not participate in the secondary reaction.

As components of the secondary reaction, one employs preferably a dye from the group of the quinoid dyes, especially preferred are toluidine blue, methylene blue, toluidine red, Nile blue A or Rhodamine GG. Additionally, one employs preferably a dye from the group of the azo dyes, especially preferred are Trypan blue, calconcarboxylic acid and methyl red.

One can preferably achieve the selectivity of the invented method to hydrogen peroxide or peroxides in that one combines the primary reaction and the secondary reaction in such a manner that the desired selectivity is achieved.

The invented method can be used in many manners and used in many areas, for example, as a sterilization indicator, in an analytical test kit for qualitative analysis in waters and chemical and as a cuvette test for the quantitative determination in waters.

Article of the invention is also a composition for the qualitative and quantitative analysis of peroxides, in particular hydrogen peroxides, in gases and liquids. This composition can serve for the qualitative, just as also for the quantitative analysis and also a combination of the both of these, according to what is desired.

This composition contains the above described components and also the components described further below for the primary reaction and the secondary reaction and therefore contains the titanium or iron compound described in the scope of the present documents and the dye.

It is also possible to formulate this composition such that the components for the primary reaction are separated from the components of the secondary reaction. These components are united with each other then at a suitable time, for example, shortly before conducting an analysis of peroxides.

Expediently, one combines the invented composition with the components, from which one can produce a common organic and/or inorganic matrix. For this type of matrix one is dealing with preferably a printing matrix or an indicator ink. For the fabrication of this type of printing matrix or indicator ink one can use common starting components that are designed for this. Common additives, thinners, solvents and printing aids belong to this group. Additionally, retarding agents, matting agents, etc. also belong to this. In this manner one can employ, for example, a screen-printing ink, and correspondingly, a screen-printing aid with the description Thermojet from the Proell company as a printing aid, and correspondingly, for the production of the printing matrix and indicator inks. Here one is dealing with a solution of polyacrylate resins and vinylchloride copolymers in organic solvents.

Preferably, the following individual components can be employed at the amounts mentioned below in the invented composition which represents a printing matrix, or correspondingly, printing ink or indicator ink:

1-30% by weight titanium oxide sulfate – sulfuric acid complex hydrate

0.01-10% by weight toluidine blue

0.5-20% by weight ammonium iron(II)sulfate hexahydrate

0.01-10% by weight indanthrene yellow 4GF

0-40% by weight thinner 2090 from Proell LLC

0-95% by weight printing aid Thermojet from Proell LLC

0-20% by weight printing aid curative PURZK 2.

The percentages by weight are related here to the total weight of the finished composition.

Article of the invention is also a testing device for the qualitative and/or quantitative determination of peroxides, in particular hydrogen peroxide in gases and liquids. With this testing device one is dealing preferably with a testing strip. The invention will be explained more closely in the following with reference to this testing strip.

The testing strip has a substrate, said substrate represents a common substrate for these type of testing strips. Polyester film, PE and PP film, or correspondingly, uncoated and coated paper are used depending on the application area.

An inventive composition in the form of a printing matrix is printed onto this substrate. A finished screen printing ink can be used as a corresponding foundation for the invented composition and therefore also for the testing strip. However, other printing matrices can also work in this application. This printing matrix is preferably applied to the substrate with a screen-printing process. After the substrate matrix, or correspondingly, the indicator ink has been

printed onto the substrate or carrier material, in applications in the clinical area a clear coat is applied onto the composition for protection.

In choosing the printing matrix one should pay attention that the access of the peroxides and the hydrogen peroxide to the reactive components is not restricted. Dampness retaining media can also be added, for example D(-) sorbite or magnesium chloride.

The invented articles are described more closely through the following examples which exemplify the preferred embodiments.

Example 1:

Quantitative analysis of hydrogen peroxide in aqueous systems:

For the reaction solutions the following is preferred:

1. 0.005% by weight toluidine blue (Fluka AG No. 52040) in 1M sulfuric acid solution
2. 0.05% by weight titanium oxide sulfate – sulfuric acid complex hydrate (Aldrich Chem. N., 33, 398-0) in 1M sulfuric acid solution.

5 ml of the reaction solution 1 are mixed together with 1 ml of the reaction solution 2 to an analytical composition and mixed with 0.2 ml of a hydrogen peroxide containing sample for the analysis of the hydrogen peroxide concentration in the concentration range between 1-10 mg/l. The solution is measured photometrically at 633 nm after a waiting period of 30 minutes at 75°C.

Example 2:

Qualitative analysis of hydrogen peroxide in aqueous systems:

The following are prepared as reaction solutions:

1. 4% by weight ammonium iron (II) sulfate hexahydrate (Fluka AG No. 09721) in water
2. 0.08% by weight methylene blue (Fluka AG No. 66720) in water

The reaction solutions 1 and 2 are mixed at a ratio of 20:1 for the fabrication of the analytical composition. A solution that is to be investigated for hydrogen peroxide is mixed at about 1:1 with the analytical composition. The color change from blue to orange, and correspondingly, to brown indicates a hydrogen peroxide concentration of over 0.01% in the analyte.

Example 3:

Fabrication of a testing strip for the quantitative and/or qualitative analysis of hydrogen peroxide in the gaseous phase:

The following reagents are mixed together to produce a composition for the quantitative and/or qualitative analysis of hydrogen peroxide:

11.7% by weight	titanium oxide sulfate – sulfuric acid complex hydrate (Aldrich Chem. Co. 33, 398-0)
0.2% by weight	toluidine blue (Fluka AG No. 52040)
26.8% by weight	retarding agent V6604 (Proell LLC; solvent mixture)
58.4% by weight	printing aid Thermojet (Proell LLC)
<u>2.4% by weight</u>	silica
100	

This composition, which represents a type of indicator ink, is printed via screen-printing onto a testing strip.

If one exposes this type of testing strip to a hydrogen peroxide concentration of 6 mg/l in the gaseous phase, then the testing strip changes its color over time from blue to green, then to yellow. Thus, the testing strip is integrated over time.

In the case of an exposure time of 30 minutes, the testing strip indicates a variation of the hydrogen peroxide concentration in the range of 1-10 mg/l through a color change of blue to green, then to yellow. For the quantitative analysis this color change can be analyzed with reflectometry.

Example 4:

Fabrication of a testing strip for the quantitative and/or qualitative analysis of hydrogen peroxide in the gaseous phase:

One fabricates a testing strip as described in example 3, where the following reagents are used:

8% by weight	ammonium iron(II) sulfate hexahydrate (Fluka AG No. 09721)
1% by weight	toluidine blue (Fluka AG No. 52040)
16% by weight	thinner 2090 (Proell LLC)
68% by weight	printing aid Thermojet (Proell LLC)
<u>7% by weight</u>	printing aid PURZK 2 (Proell LLC, isocyanate)
100	

If one exposes this type of testing strip to a hydrogen peroxide concentration of 6 mg/l in the gaseous phase, then the testing strip changes its color over time from blue to green, then to brown. Thus, the testing strip is integrated over time.

In the case of an exposure time of 30 minutes, the testing strip indicates a variation of the hydrogen peroxide concentration in the range of 1-10 mg/l through a color change of blue to green, then to brown. For the quantitative analysis this color change can be analyzed with reflectometry.

Example 5:

Fabrication of a testing strip for the quantitative and/or qualitative analysis of hydrogen peroxide in the gaseous phase:

One fabricates a testing strip as described in example 3, where the following reagents are used:

11.7% by weight	titanium oxide sulfate – sulfuric acid complex hydrate
0.08% by weight	toluidine blue
0.12% by weight	indanthrene yellow (BASF)
26.8% by weight	retarding agent V6604 (Proell LLC; solvent mixture)
58.4% by weight	printing aid Thermojet (Proell LLC)
<u>2.9% by weight</u>	silica
100	

If one exposes this type of testing strip to a hydrogen peroxide concentration of 6 mg/l in the gaseous phase, then the testing strip changes its color over time from green to yellow. Thus, the testing strip is integrated over time.

In the case of an exposure time of 30 minutes, the testing strip indicates a variation of the hydrogen peroxide concentration in the range of 1-10 mg/l through a color change from green to yellow.

Example 6:

Dye decomposition reaction with time and peroxide concentration dependence:

For the composition described in example 1, the dye's decomposition as a function of peroxide concentration is shown graphically in Figure 1, and the dye's decomposition as a function of time and temperature is reported graphically in Figure 2.

As Figure 1 shows, the peroxide induced dye decomposition at constant temperature and at constant exposure time is a function of the peroxide concentration. Thus, this dye decomposition reaction is suited as an indicator of a specified peroxide concentration falling below its rated level.

In addition to the depicted decomposition of a blue color, there is an increase in a yellow color such that altogether a color change is observed from blue to green, then to yellow.

As Figure 2 shows, the dye decomposition reaction is additionally time dependent. In Figure 2 the dye decomposition reaction is graphically represented as a function of time and temperature. The dye decomposition is therefore a measure of the peroxide exposure time. The dye decomposition reaction is temperature dependent at constant peroxide exposure time. The dye decomposition is therefore a measure of the temperature. Hence, the dye decomposition reaction can be used as an indicator of a specified exposure time and of a specified exposure temperature falling below their rated levels.

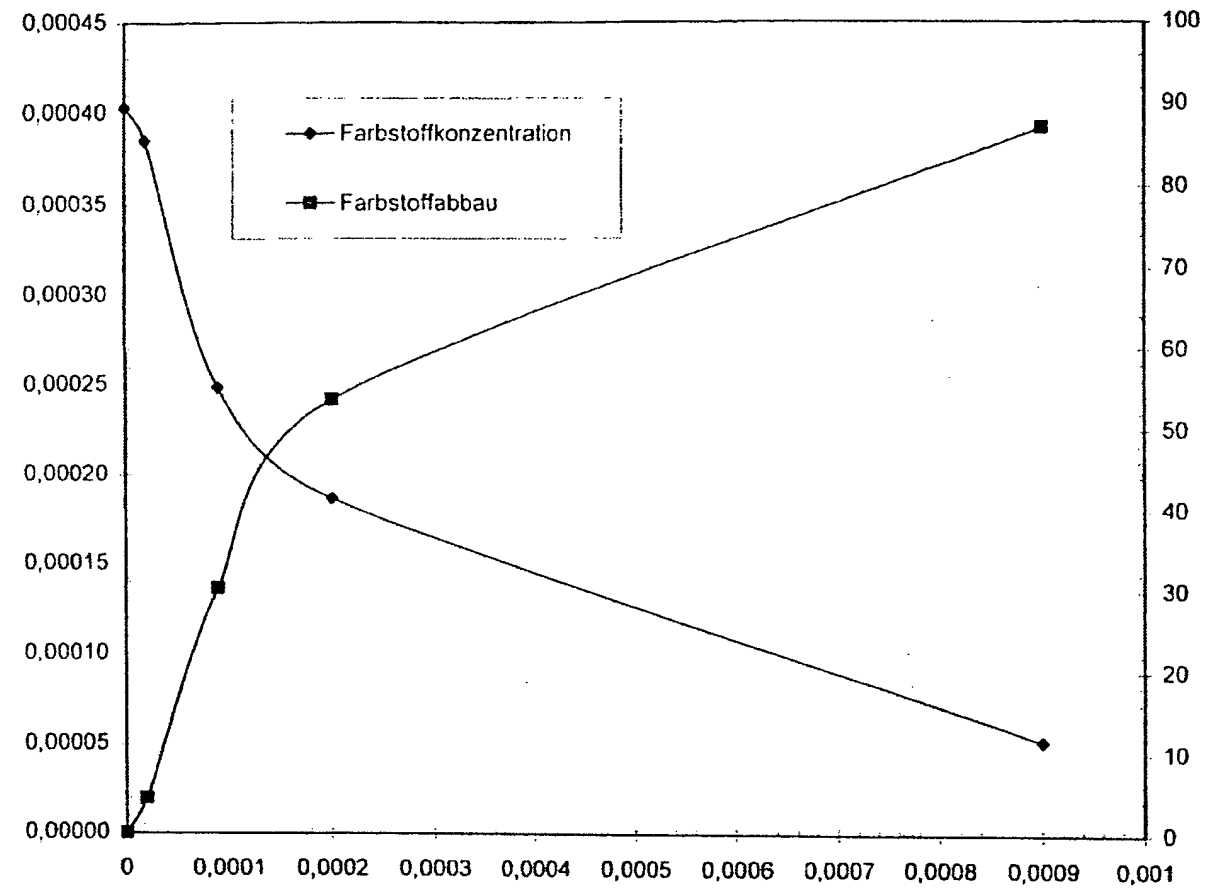
If one adds another dye to the invented composition, where said dye cannot be decomposed, then the reaction zone of the invented testing strip retains the color of the additional dye that cannot be decomposed, said color differs from the starting color. In lieu of a dye a pigment can also be used successfully here. Through this, every type of starting color and final color can be realized, compare example 5.

Patent Claims

1. Method for the qualitative and quantitative determination of peroxides, in particular of hydrogen peroxide, in gases and liquids with the use of an analytical reaction that consists of two steps is characterized in that, in the first step hydrogen peroxide or another peroxide is reacted with a titanium or iron compound to a reaction product and in the second step this reaction product enters in a decomposition reaction with a dye.
2. Method according to claim 1 is characterized in that an inorganic titanium(IV) compound and in particular titanium(IV) oxide sulfate – sulfuric acid complex hydrate is employed as the titanium compound, and an inorganic iron(II) compound, in particular ammonium iron(II) sulfate hexahydrate is employed as the iron compound, and a quinoid dye or an azo dye or a mixture of two or more dyes, chosen from the group consisting of quinoid dyes and azo dyes are employed as the dye for the dye decomposition reaction.
3. Method according to claim 2 is characterized in that toluidine blue, methylene blue, toluidine red, Nile blue A or Rhodamine GG are employed as the quinoid dye and trypan blue, calconcarboxylic acid or methyl red are employed as the azo dye.
4. Method according to one of the previous claims is characterized in that the components of the first and second steps are embedded in an organic and/or inorganic matrix in order to produce a dry reaction zone.
5. Method according to one of the previous claims is characterized in that the method is used for the detection/analysis of hydrogen peroxide including hydrogen peroxide vapor in sterilization setups.
6. Composition for the qualitative and quantitative analysis of peroxide, in particular hydrogen peroxide, in gases and liquids is characterized in that the composition contains a titanium or iron compound, which reacts in the first step with hydrogen peroxide or with another peroxide to form a reaction product, and the composition contains a dye, which reacts in the second step with this reaction product in a decomposition reaction.
7. Composition according to claim 6 is characterized in that the composition contains an inorganic titanium(IV) compound and in particular titanium(IV) oxide sulfate – sulfuric acid complex hydrate as the titanium compound, and it contains an inorganic iron(II) compound, in particular ammonium iron(II) sulfate hexahydrate as the iron compound and it contains a quinoid dye or an azo dye and in particular a quinoid or azo dye described in claim 3 or a mixture of two or more dyes chosen from the group consisting of those type of quinoid and azo dyes.
8. Composition according to claim 6 or 7 is characterized in that the composition is incorporated into an organic and/or inorganic matrix which can serve, in particular, for producing a dry reaction zone.
9. Composition according to claim 8 is characterized in that for the matrix one is dealing with a printing matrix or an indicator ink and that the composition contains, in order to produce this type of matrix or indicator ink, a common additive, thinner, solvent or printing aid or a mixture of one or several of these common additives, thinners, solvents or printing aids.
10. Testing device, in particular testing strips, for the qualitative and quantitative determination of peroxides, in particular of hydrogen peroxide in gases and liquids with the use of an analytical reaction that consists of two steps and with a substrate made of a polymeric film or made out of coated or uncoated paper is characterized in

that a composition is printed onto the substrate according to one of the claims 6 to 8 and in particular is covered with a clear coat.

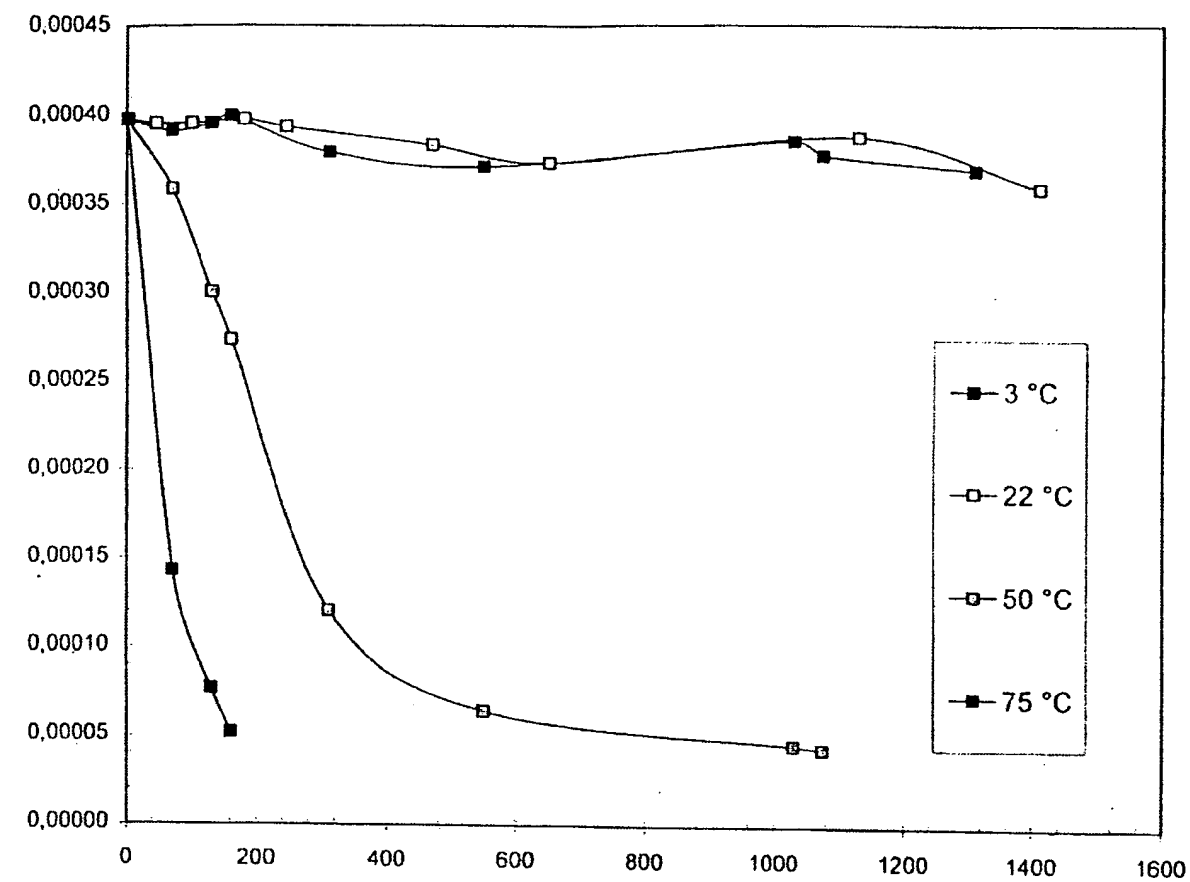
Figure 1: Dye decomposition as a function of the peroxide concentration



left axis: dye concentration
right axis: dye decomposition
x axis: peroxide concentration

legend: dye concentration
dye decomposition

Figure 2: Dye decomposition as a function of time and temperature



left axis: dye concentration
x axis: time (minutes)